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(19) (CA) **CANADIAN PATENT** (12)

(54) Method of Producing Level Off D P Microcrystalline  
Cellulose and Glucose From Lignocellulosic Material

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**Canada**

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A METHOD OF PRODUCING LEVEL OFF DP MICROCRYSTALLINE  
CELLULOSE AND GLUCOSE FROM LIGNOCELLULOSIC MATERIAL.

ABSTRACT

Microcrystalline cellulose has many applications in the pharmaceutical, food, paper and structural composite industries. Level off DP (Degree of Polymerization) microcrystalline cellulose is made up of a chain of about 250 glucose molecules in the form of a microcrystal. In nature, several microcrystals are hinged together and surrounded by amorphous cellulose to form a cellulose microfibril. If the amorphous cellulose is removed, the resultant product is called level off DP (degree of polymerization) microcrystalline cellulose. When lignocellulosic material is processed according to applicant's earlier processes (Canadian Patents 1,096,374 and 1,141,376), the dissociated material is partitioned by removing the lignin and the xylan leaving a low DP ( 320) cellulose fraction. This material can be converted to level off DP microcrystalline cellulose and glucose by soaking the cellulose in an acid solution, dewatering it, returning the acid impregnated cellulose to the reactor, introducing high

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pressure steam (300-700 psi) and when substantially all of the material reaches a temperature of the order of 215 degrees celcius, releasing it instantly to atmosphere. This procedure will produce a mixture of level off DP microcrystalline cellulose and glucose. If the temperature of the material is allowed to reach a uniform temperature of 234 degrees celcius plus a small allowance for measurement error, before instant release to atmosphere, the procedure will produce substantially all glucose.

This invention relates to a method of producing level off DP microcrystalline cellulose and glucose from lignocellulosic material.

More particularly, this invention relates to the use of an explosive depressurization reactor for the production of level off DP microcrystalline cellulose and glucose from lignocellulosic material. Until my inventions to render lignin separable from cellulose and hemicellulose and the product so produced (Canadian Patents 1,096,374 and 10 1,141,376), there was no known economically viable process to cleanly separate undegraded and chemically reactive lignin and the hemicellulose from the cellulose in lignocellulosic material. Thus, until now, acid hydrolysis of lignocellulosic biomass has been done by treating the material as a composite.

Lignocellulosic biomass is comprised of three main chemical components -- lignin, hemicellulose and cellulose -- in the following approximate proportions, plus ash and trace elements:



## Hardwoods:

Lignin 21%

Hemicellulose 24%

Cellulose 48%

## Annual Plant Material (Straw, Bagasse etc.):

Lignin 15%

Hemicellulose 32%

Cellulose 46%

10       The cellulose and hemicellulose are both carbohydrates. Cellulose is nature's most abundant chemical. Hemicellulose is second, Lignin is third. Cellulose is comprised of six-carbon (glucose) sugar molecules. The xylan component (approximately 70%) of the hemicellulose in annuals and hardwoods is comprised mainly of five-carbon (xylose) sugar molecules. The lignin is a complex amorphous molecule comprised of many of the elements found in oil and gas such as phenol, benzene, propane, etc. The function of these three materials in the lignocellulosic complex is as follows:

20       - The core of the lignocellulosic fibre is comprised primarily of cellulose. Cellulose is the skeleton in the fibre structure. It occurs as crystalline bundles which support the fabric of the tree or plant.

- The hemicellulose and lignin are cross-linked to, form a matrix which surrounds the cellulose skeleton and holds the structure together in the manner of resin in a fibreglass composite.

It is this lignin/hemicellulose matrix which provides nature's protection against microbial invasion. It also renders the material water resistant.

10 With the application of the above referenced patents, the problem, which has baffled scientists and engineers for more than a century, of how to break the intermolecular cross-links between the lignin and the hemicellulose without causing substantial degradation to either of these chemical components has been solved. Once the intermolecular cross-links in the lignocellulosic material have been severed, it is relatively simple to partition the material into its three main chemical components (lignin, hemicellulose and cellulose) using mild non-reactive solvents.

The process accomplishes this by:

20 - Rapidly heating the material (less than 60 seconds) with high pressure (400 to 700 psi) steam to its structural failure temperature and then releasing it instantaneously to atmospheric pressure. The powerful mechanical action of the resulting explosion fractures the structurally weakened (like softened spot welds) lignin/hemicellulose

intermolecular cross-links causing the biomass to be transformed into a mixture of lignin, hemicellulose and, cellulose.

- Extracting the lignin from the mixture using a mild organic solvent such as ethanol, methanol or a weak sodium hydroxide solution at room temperature, then after filtering

- Separating the remaining material into cellulose and hemicellulose fractions by dissolving the hemicellulose in a weak (1 wt.%) solution of sodium hydroxide at 50 degrees celcius to 100 degrees celcius dependent on the desired  
10 extraction time.

Alternatively, these last two steps can be accomplished by:

- Extracting the hemicellulose from the whole exploded material with warm water at 50 degrees celcius for two hours, then after filtering,

- Extracting the lignin using a mild organic solvent such as ethanol, methanol or a mild (0.1N) solution of sodium hydroxide at room temperature, which after filtering  
20 leaves a high purity cellulose fraction.

The resulting fractions (chemical components) are very pure and largely occur in so-called native or

undegraded form. The lignin is amorphous and very delicate chemically when it is isolated from the hemicellulose matrix. It will hydrolyse easily in a mild acid solution at or below its glass transition temperature around 125 degrees celcius, dependent on moisture content. Similarly, the xylan component of the hemicellulose is also amorphous and only slightly more rugged chemically than the lignin. It will hydrolyse quite easily in a mild acid solution at its glass transition temperature at or around 165 degrees celcius, also dependent on moisture content. The crystalline component of the cellulose, on the other hand, is more rugged chemically and significantly more difficult to hydrolyse than the other two, but, it will hydrolyse quite readily in a mild acid solution at or slightly above its glass transition temperature of 234 degrees celcius.

When the lignocellulosic material is acid hydrolysed as a composite, the acid reacts initially with the more delicate amorphous (lignin and xylan) components. Before the crystalline cellulose is hydrolysed, they are degraded beyond economic value as a chemical feedstock to what is commonly called a black liquor, and they mix intimately with the glucose creating toxicity and a difficult separation problem. Moreover, because the microstructure of the composite is resistant to water and other liquids, the wood chip or other untreated feedstock will resist the penetration of the acid and will therefore tend to hydrolyse from the outside of the chip toward the centre. Thus, the glucose which is first produced from the outside of the chip is degraded before the glucose from the



inside of the chip is released. This is the fundamental reason why yields of glucose by acid hydrolysis of lignocellulosic materials have until now been limited to below 50% of theoretical.

A cellulose microfibril is made up of a cellulose microcrystal surrounded by and hinged to the next microcrystal by an amorphous region of cellulose. It has now been found that this amorphous cellulose will hydrolyse to glucose under less harsh hydrolysis conditions of time, temperature, and acid concentration than is required to hydrolyse the microcrystal to glucose. For this reason, under the proper hydrolysis conditions, it has now been found that it is possible to produce microcrystalline cellulose in a glucose solution.

According to the present invention there is provided a method of producing level off DP microcrystalline cellulose and glucose from lignocellulosic material, comprising:

(a) packing the lignocellulosic material in a divided, exposed, moist form in a pressure vessel having a closed extrusion die outlet,

(b) rapidly filling the pressure vessel with steam at a pressure of at least 500 psi to bring by means of the pressurized steam, substantially all of the lignocellulosic material to a temperature in the range 185 degrees celcius to

240 degrees celcius in less than 60 seconds to thermally soften the lignocellulosic material into an extrudable condition, and

(c) As soon as the said extrudable condition has been attained, opening the extrusion die outlet and instantly extruding the lignocellulosic material in the said extrudable condition, from the pressure vessel through the extrusion die outlet to atmosphere, so that the said material issues from the extrusion die in particulate form with lignin therein rendered into particles substantially in the range 1 to 10 microns and separable from the cellulose and hemicellulose; the particulate lignin, hemicellulose and cellulose being together in dissociated form and having the appearance of potting soil, a major portion of the lignin being soluble in methanol or ethanol and being thermoplastic, the cellulose being in the form of crystalline alpha cellulose microfibrils and suitable for digestion or conversion by micro-organisms and enzymes,

(d) partitioning the lignin, hemicellulose and cellulose in the particulate material,

(e) soaking the partitioned cellulose in an acid solution of at least one acid selected from the group consisting of sulphuric acid, hydrochloric acid and sulphur dioxide until the acid is distributed evenly throughout the partitioned cellulose, and then reducing the moisture content of the partitioned cellulose to below 50% with the

cellulose impregnated with acid at a concentration in the range 0.05% to 2.0% of the weight of the cellulose,

(f) packing the acid impregnated cellulose once more into a pressure vessel having a closed extrusion die outlet,

(g) rapidly filling the pressure vessel with steam to a pressure in the range 300 psi to 700 psi to bring, by means of the pressurized steam, substantially all of the acid impregnated cellulose to a temperature in the range of 185 degrees celcius to 240 degrees celcius in less than 60 seconds, and thereby weaken by hydrolysis and thermal softening, the intramolecular bonds joining the glucose units to form the cellulose, then

(h) opening the extrusion die outlet, and instantly extruding the acid impregnated cellulose from the pressure vessel through the extrusion die to atmospheric pressure, thereby breaking the intramolecular cross-links in the cellulose to depolymerize the hydrolysed, acid impregnated cellulose to produce a mixture of cellulose and a glucose solution therefrom, and rapidly reducing the temperature of the extruded material to below 100 degrees celcius to prevent further depolymerization of the cellulose and degradation of the glucose, and then

(i) neutralizing the acidity of the glucose solution and residual cellulose.

Thus it has now been found, according to the present invention, that using the above referenced inventions, the partitioned cellulose is in the form of cellulose fibrils which are small in size (20-50 microns in diameter one or two millimetres in length) and expanded by the mechanical action of the explosive decompression leaving voids where the lignin and hemicellulose once resided and where acid selected from the groups consisting of; sulphuric acid, hydrochloric acid or sulphur dioxide can easily penetrate. It has further been found, according to the present invention, that when the cellulose is damp with moisture, an acid pre-soak will wick and thereby distribute the acid evenly onto each molecule of cellulose throughout the material. By this means the problem of accessibility is solved.

In some embodiments of the present invention the acid impregnated cellulose may be dewatered to a moisture content in the range 20% to 40%. This dewatered acid impregnated cellulose may then be loaded into the explosive decompression reactor, charged with high pressure steam at pressures between 300 psi and 700 psi, depending on moisture content, to bring the material to a temperature between 185 degrees celcius and 240 degrees celcius, in less than 60 seconds, preferably less than 45 seconds depending on the temperature and acid concentration. When the desired temperature is reached the acid impregnated cellulose is instantly discharged to atmospheric pressure. Preferably any residual cellulose is filtered from the glucose solution.

In some embodiments of the present invention wherein the neutralized end product is a mixture of glucose from the amorphous component of the cellulose and level off DP microcrystalline cellulose from the crystalline alpha cellulose fraction of the cellulose, the cellulose is impregnated with acid at a concentration of 0.05% to 1.0% of the weight of the cellulose, and the pressure vessel is rapidly filled with steam to a pressure between 350 psi and 550 psi to bring the acid impregnated cellulose to a  
10 temperature in the range of 200 degrees celcius to 225 degrees celcius in less than 60 seconds and then discharged instantly to atmospheric pressure.

In other embodiments of the present invention wherein the neutralized end product is a mixture of glucose from the amorphous component of the cellulose and level off DP microcrystalline alpha cellulose from the crystalline alpha cellulose fraction of the cellulose, the cellulose is impregnated with hydrochloric acid at a concentration of about 0.2% of the weight of the cellulose, and the pressure  
20 vessel is rapidly filled with steam to a pressure of about 450 psi to bring the acid impregnated cellulose to a temperature of about 215 degrees celcius in less than 45 seconds and then discharged instantly to atmospheric pressure.

In yet other embodiments of the present invention wherein the end product is substantially all glucose, the pressure vessel is rapidly filled with steam to a pressure in the range 550 psi to 700 psi, to bring the cellulose, which has been impregnated with acid to a level in the range 0.5% to 1.5% of the weight of the cellulose, to a temperature in the range 215 degrees celcius to 240 degrees celcius, in less than 60 seconds and then discharged instantly to atmospheric pressure.

10           In other embodiments of the present invention wherein the end product is substantially all glucose, the pressure vessel is rapidly filled with steam to a pressure of about 650 psi to bring the cellulose, which has been impregnated with sulphuric acid to a level of about 1.0% of the weight of the cellulose, to a temperature of about 234 degrees celcius, in less than 45 seconds.

          Preferably, condensate, which is produced when the high pressure steam contacts the relatively cool cellulosic material, is removed from the bottom of the pressure vessel  
20   as it is formed.

          Any residual cellulose may be treated with enzymes for the conversion thereof to glucose or retreated in the explosion decompressure reactor.

The accompanying Figure 1. is provided to describe, by way of example, embodiments of the present invention. Figure 1 is a sectional sideview of a pressure vessel having an extrusion die outlet.

In Figure 1, there is shown a pressure vessel 2, an extrusion die outlet 6, an extrusion die closure plug 30, a loading end closure flap 8, and steam inlet orifices 10 to 12. The pressure vessel 2 has a bottleneck portion 14 leading to the die 4 and entry ports 16 and 18 for  
10 temperature probes (not shown).

The front end of the pressure vessel 2, containing the die outlet 14, has a flange 20 to which is sealed a curved impinging tube 22 which gradually reduces in cross-section in a downstream direction. The curved impinging tube 22 has a spindle inlet sleeve 24 provided with a flange 26. A pneumatic ram 28 is attached to the flange 26 and has a die closure plug 30 mounted on the spindle 32 of the ram 28. A condensate drainage tank 31 is provided having an outlet valve 33.

20 The rear end 34 of the pressure vessel 2 is sealed to the remainder by flanges 36 and 38 and has the loading end closure flap 8 hinged thereto by a hinge 40 and sealable therewith by a clamp 42. The rear end 34 has a venting safety valve 44.

In operation, the loading end closure flap 8 is opened and the pressure vessel 2 is loaded with cellulose impregnated with at least one acid selected from the group consisting of sulphuric acid, hydrochloric acid or sulphur dioxide, with the die closure plug 30, and the valve 33 closed.

10 With the pressure vessel 2 completely filled with acid impregnated cellulose, the die closure plug 30 is sealed by the pneumatic ram 28 and the closure plug 8 is sealed to the rear end 34, by the clamp 42, and then the pressure vessel is filled with steam at a pressure between 300 psi and 700 psi, to bring the cellulose to a temperature between 185 degrees celcius and 240 degrees celcius, in less than 60 seconds, preferably less than 45 seconds, depending on the moisture content of the material and the pH of the acid solution impregnated in the cellulose. The temperature probes (not shown) in the ports 16 and 18 are used to monitor the temperature of the acid impregnated cellulose to determine when the cellulose has reached the chosen  
20 temperature.

As soon as the cellulose in the pressure vessel has reached the desired temperature, the extrusion die outlet is opened and the material is instantly extruded from the pressure vessel through the extrusion die outlet to atmosphere.



The percentage of acid used in the impregnation step will depend on the temperature to be used, the time to achieve that temperature and the moisture content of the impregnated cellulose. In any case, acid concentration will be no more than two percent of the dry weight of the material, and usually much less. The object of the process is to weaken by acid hydrolysis and heat, the intramolecular bonds joining the glucose units to form the cellulose. The combination of the acid hydrolysis and the mechanical shock caused by the instant decompression and the extrusion through the die will fracture those bonds, producing a high concentration of glucose and at the same time reducing the pressure to atmosphere, thus reducing the temperature to below 100 degrees celcius, which will quench further chemical hydrolysis.

The resulting product can then be neutralized by a suitable base and filtered to remove the residual cellulose which can be used as described above or returned to the pressure vessel for a second treatment or passed to an enzymatic hydrolysis process to complete the conversion to glucose.

During the first few seconds after the steam is introduced into the reactor, contact with the relatively cool cellulosic material produces a liquid condensate. This condensate covers between 10 and 30 percent of the cellulosic material depending on the moisture content and

the starting temperature of the cellulose feedstock, thus preventing proper processing of the submerged cellulosic material. The tank 31 for removing that condensate, as it is formed, substantially improves the performance of the process.

## Claims:

1. A method of producing level off DP microcrystalline cellulose and glucose from lignocellulosic material, comprising:

(a) packing the lignocellulosic material in a divided, exposed, moist form in a pressure vessel having a closed extrusion die outlet,

(b) rapidly filling the pressure vessel with steam at a pressure of at least 500 psi to bring by means of the pressurized steam, substantially all of the lignocellulosic material to a temperature in the range 185 degrees celcius to 240 degrees celcius in less than 60 seconds to thermally soften the lignocellulosic material into an extrudable condition, and

(c) as soon as the said extrudable condition has been attained, opening the extrusion die outlet and instantly extruding the lignocellulosic material in the said extrudable condition, from the pressure vessel through the extrusion die outlet to atmosphere so that the said material issues from the extrusion die in particulate form with lignin therein rendered into particles substantially in the range 1 to 10 microns and separable from the cellulose and hemicellulose, the particulate lignin, hemicellulose and

cellulose being together in dissociated form having the appearance of potting soil, a major portion of the lignin being soluble in methanol or ethanol and being thermoplastic, the cellulose being in the form of crystalline alpha cellulose microfibrils and suitable for digestion or conversion by micro-organisms and enzymes,

(d) partitioning the lignin, hemicellulose and cellulose in the particulate material,

(e) soaking the partitioned cellulose in an acid solution of at least one acid selected from the group consisting of sulphuric acid, hydrochloric acid and sulphur dioxide until the acid is distributed evenly throughout the partitioned cellulose, and then reducing the moisture content of the partitioned cellulose to below 50% with the cellulose impregnated with acid at a concentration in the range 0.05% to 2.0% of the weight of the cellulose,

(f) packing the acid impregnated cellulose once more into a pressure vessel having a closed extrusion die outlet,

(g) rapidly filling the pressure vessel with steam to a pressure in the range 300 psi to 700 psi to bring, by means of the pressurized steam, substantially all of the acid impregnated cellulose to a temperature in the range of 185 degrees celcius to 240 degrees celcius in less than 60 seconds, and thereby weaken by hydrolysis and thermal

softening, the intramolecular bonds joining the glucose units to form the cellulose, then

(h) opening the extrusion die outlet, and instantly extruding the acid impregnated cellulose from the pressure vessel through the extrusion die to atmospheric pressure, thereby breaking the intramolecular cross-links in the cellulose to depolymerize the hydrolysed, acid impregnated cellulose to produce a mixture of cellulose and a glucose solution therefrom, and rapidly reducing the temperature of the extruded material to below 100 degrees celcius to prevent further depolymerization of the cellulose and degradation of the glucose, and then

(i) neutralizing the acidity of the glucose solution and residual cellulose.

2. A method according to claim 1, wherein any residual cellulose is filtered from the glucose solution

3. A method according to claim 1, wherein the acid impregnated cellulose is dewatered to a moisture content in the range 20% to 40% before being packed once more into a pressure vessel.

4. A method according to claim 1, wherein the end product is a mixture of glucose from the amorphous component of the cellulose and level off DP microcrystalline cellulose from the crystalline alpha cellulose fraction of the

cellulose, and the cellulose is impregnated with acid at a concentration of 0.05% to 1.0% of the weight of the cellulose, and the pressure vessel is rapidly filled with steam to a pressure between 350 psi and 550 psi to bring the acid impregnated cellulose to a temperature in the range of 200 degrees celcius to 225 degrees celcius in less than 60 seconds.

5. A method according to claim 1, wherein the end product is a mixture of glucose from the amorphous component of the cellulose and level off DP microcrystalline alpha cellulose from the crystalline alpha cellulose fraction of the cellulose, and the cellulose is impregnated with hydrochloric acid at a concentration of about 0.2% of the weight of the cellulose, and the pressure vessel is rapidly filled with steam to a pressure of about 450 psi to bring the acid impregnated cellulose to a temperature of about 215 degrees celcius in less than 45 seconds.

6. A method according to claim 1, wherein the end product is substantially all glucose, the pressure vessel is rapidly filled with steam to a pressure in the range 550 psi to 700 psi, to bring the cellulose, which has been impregnated with acid, to a level in the range 0.5% to 1.5% of the weight of the cellulose, to a temperature in the range 215 degrees celcius to 240 degrees celcius, in less than 60 seconds.

7. A method according to claim 1, wherein the end product is substantially all glucose, the pressure vessel is rapidly filled with steam to a pressure of about 650 psi to bring the cellulose, which has been impregnated with acid to a level of about 1% of the weight of the cellulose, to a temperature of about 234 degrees celcius, in less than 45 seconds.

8. A method according to claim 1, wherein liquid condensate is removed from the bottom of the pressure vessel as it is formed.

9. A method according to claim 1, wherein steps (e) to (i) are repeated on any residual cellulose.

10. A method according to claim 1, wherein any residual cellulose is treated with enzymes for the conversion thereof to glucose.



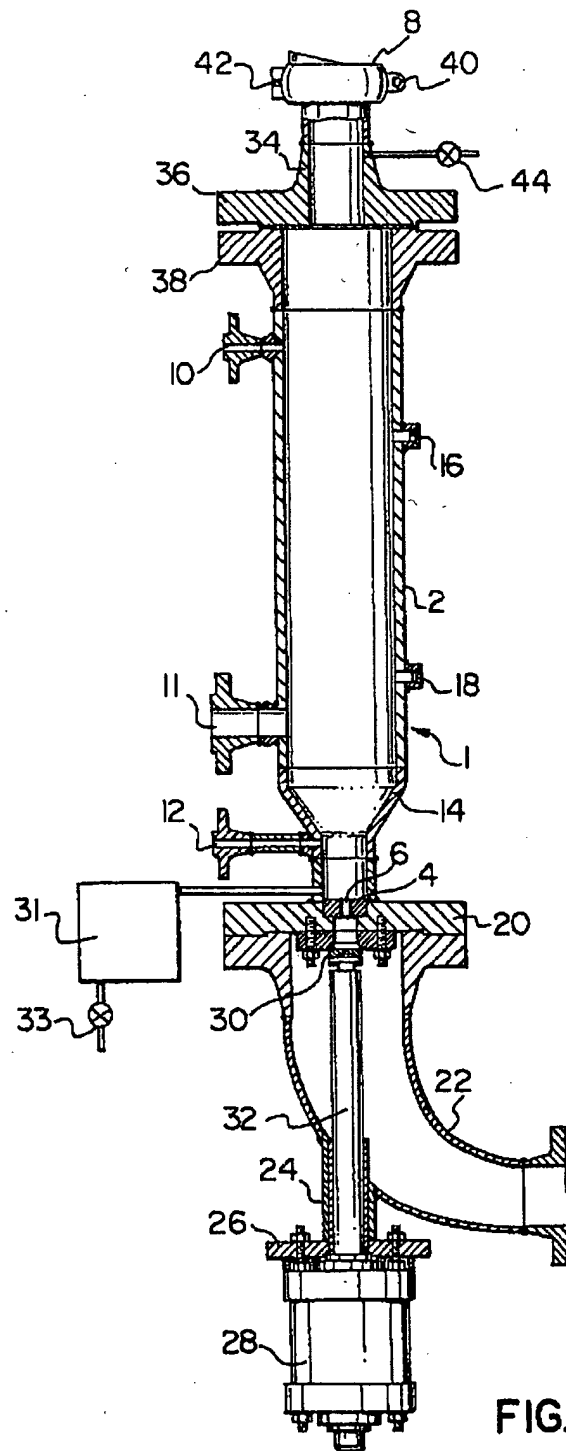


FIG. 1

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